

# Structural Stability of $\text{Li}_{1-x}\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$ Cathodes Under Mild Heat

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## Introduction

Among the known transition metal oxide cathodes, the layered  $\text{LiCoO}_2$  has become the leading candidate for lithium-ion cells. However,  $\text{LiCoO}_2$  has a limited practical capacity of 140 mAh/g corresponding to a reversible extraction/insertion of 0.5 lithium ion per transition metal ion. Also, cobalt is relatively toxic and expensive. These considerations have created enormous interest in the development of alternate cathode materials. In this regard, the layered lithium nickel oxide with a small amount of cobalt,  $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$ , has become appealing as it exhibits a higher practical capacity of about 180 mAh/g corresponding to a reversible extraction/insertion of 0.65 lithium per transition metal ion.<sup>1</sup> Our group showed recently that the  $\text{Li}_{1-x}\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  cathodes obtained by a chemical extraction of lithium from  $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$ , however, experience a decrease in the  $c/a$  ratio on heating at mild temperatures  $T > 50^\circ\text{C}$  due to the migration of nickel ions from the transition metal ion planes to the lithium planes.<sup>2</sup> We present here the structural characterization of electrochemically charged and cycled  $\text{Li}_{1-x}\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  cathodes; the characterizations are carried out after heating the charged cathodes at various temperatures for various intervals of time or after cycling at various temperatures.

## Experimental

Coin cells fabricated with  $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$  cathodes containing 20 wt% fine carbon (Denka Black) and 5 wt% polytetrafluoroethylene (PTFE) binder, metallic lithium anodes, polyethylene separator, and  $\text{LiClO}_4$  in propylene carbonate (PC)/1,2-dimethoxyethane (DME) electrolyte were charged at a constant current density of  $50\ \mu\text{A}/\text{cm}^2$  to various lithium contents  $1-x$  in  $\text{Li}_{1-x}\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$ . The cells were then opened after the first charge and the cathodes were washed with PC to remove the residual  $\text{LiClO}_4$  from the cathodes. The charged cathodes were then examined by X-ray powder diffraction before and after heating in an air-oven at various temperatures ( $50$  to  $100^\circ\text{C}$ ) for various intervals of time. Additionally, cathodes cycled at  $0.2\text{C}$  rate between  $3.2$  and  $4.3\text{ V}$  at different temperatures were also opened and examined by X-ray diffraction without subjecting to additional heat treatment in air-oven. The X-ray data were analyzed by Rietveld program to assess the structural stability.

## Results and Discussion

Figure 1 shows the X-ray diffraction patterns of  $\text{Li}_{0.27}\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  (obtained after 1<sup>st</sup> charge) after heating at  $100^\circ\text{C}$  for various intervals of time. Of particular interest is the movement of the (108) and (110) reflections towards each other on heating the charged cathode. Figure 2 shows the variations of the  $c/a$  ratios of the charged  $\text{Li}_{1-x}\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  cathodes before and after heating at various temperatures ( $50$ - $100^\circ\text{C}$ ) for various intervals of time. The data clearly reveal that the lattice parameters and the  $c/a$  ratio change on heating the charged cathodes at as low as  $50^\circ\text{C}$ . For a given degree of charge (lithium content  $1-x$ ), the magnitude of change in lattice

parameters increases as the heating temperature or time increases. Also, for a given heating temperature or time, the magnitude of change in lattice parameters increases as the degree of charge increases or the lithium content  $1-x$  in  $\text{Li}_{1-x}\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  decreases. Rietveld analysis of the X-ray diffraction data reveals that the decrease in  $c/a$  ratio on heating is due to a migration of the  $\text{Ni}^{3+}$  ions from the transition metal planes to the lithium planes. The extent of migration of nickel ions increases with increasing heating temperature and prolonged heating at much higher temperatures  $T \approx 150^\circ\text{C}$  is found to give a cubic symmetry with a  $c/a$  ratio of  $4.9$ ; the cubic sample is found to have a spinel-like structure.

X-ray diffraction analysis of the cycled cathodes also reveals a decrease in  $c/a$  ratio on cycling at higher temperatures  $T \approx 50^\circ\text{C}$ . The results reveal that the  $\text{Li}_{1-x}\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  cathodes may be prone to structural instability during long-term cycling at elevated temperatures. Similar experiments carried out with charged  $\text{Li}_{1-x}\text{CoO}_2$  cathodes under identical conditions reveal that it does not experience such a structural instability. The difference is due to a strong octahedral site stabilization energy for  $\text{Co}^{3+}$  compared to  $\text{Ni}^{3+}$ .

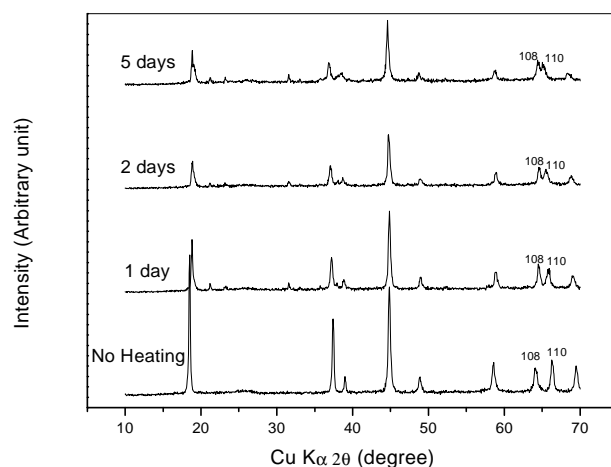


Fig.1. X-ray powder diffraction patterns of  $\text{Li}_{0.27}\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  (after 1<sup>st</sup> charge) before and after heating at  $100^\circ\text{C}$  for various intervals of time.

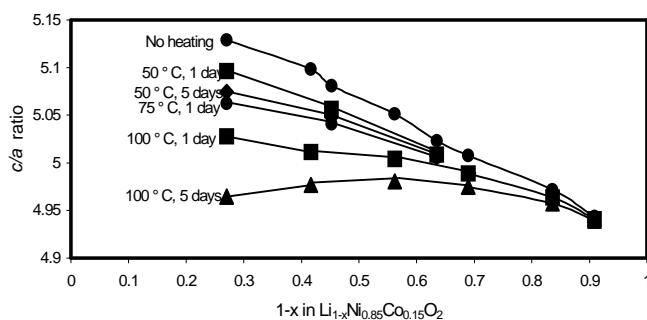


Fig. 2. Variation of  $c/a$  ratio with  $1-x$  in  $\text{Li}_{1-x}\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  (after 1<sup>st</sup> charge) before and after heating at various temperatures for various intervals of time.

## References

- W. Li and J. C. Currie, *J. Electrochem.Soc.* **144**, 2773 (1997).
- R. V. Chebiam, F. Prado, and A. Manthiram, *J. Electrochem. Soc.* **148**, A49-53 (2001).